

PCT

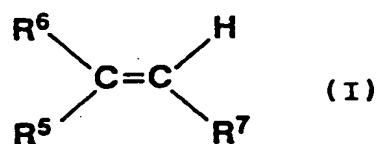
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | | |
|--|--|---|--|
| (51) International Patent Classification ⁵ : C10L 1/14, C10M 145/02 | | A1 | (11) International Publication Number: WO 94/00535 |
| | | | (43) International Publication Date: 6 January 1994 (06.01.94) |
| (21) International Application Number: PCT/EP93/01669 | | (74) Agents: MANSELL, Keith, Rodney et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB). | |
| (22) International Filing Date: 29 June 1993 (29.06.93) | | (81) Designated States: AU, BG, BR, BY, CA, CZ, FI, JP, KP, KR, KZ, NO, PL, RO, RU, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). | |
| (30) Priority data: 9213854.4 30 June 1992 (30.06.92) GB | | Published <i>With international search report.</i> | |
| (71) Applicant (for all designated States except US): EXXON CHEMICAL PATENTS INC. [US/US]; 200 Park Avenue, Florham Park, NJ 07932 (US). | | | |
| (72) Inventors; and | | | |
| (75) Inventors/Applicants (for US only) : BROWN, Gerald, Ivan [GB/GB]; 3 Orchard Gardens, West Challow, Wantage, Oxfordshire OX12 9TL (GB). DAVIES, Brian, William [GB/GB]; Pound Furlong, London Road, Blewbury, Oxfordshire OX11 9PD (GB). GOBERDHAN, Dhanesh, Gordon [GB/GB]; 22 Guy Court, King Street, Oxford OX2 6DB (GB). MORE, Iain [GB/GB]; 15 Lee Avenue, Abingdon, Oxfordshire OX14 3UT (GB). | | | |

(54) Title: ADDITIVES AND FUEL COMPOSITIONS



(57) Abstract

An additive for improving the cold flow properties of crude oil, lubricating oil or fuel oil comprises one or more oil-soluble copolymers of ethylene and an unsaturated monomer of general formula (I), wherein R⁶ is hydrogen or methyl, R⁵ is a -OOCR⁸ group wherein R⁸ is a hydrogen formate or a C₁ to C₂₈, more usually C₁ to C₁₇, and preferably a C₁ to C₈, straight or branched chain alkyl group, or R⁵ is a -COOR⁸ group wherein R⁸ is as defined above but is not hydrogen, and R⁷ is hydrogen or -COOR⁸ as defined above, and wherein (i) where there is more than one copolymer, the arithmetic mean of the content of said unsaturated monomer in the copolymers is below 11 mole %, or (ii) where there is one copolymer, the content of said unsaturated monomer in the copolymer is in the range of 6.5 to 10 mole %.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|----|--------------------------|----|--|----|--------------------------|
| AT | Austria | FR | France | MR | Mauritania |
| AU | Australia | GA | Gabon | MW | Malawi |
| BB | Barbados | GB | United Kingdom | NE | Niger |
| BE | Belgium | GN | Guinea | NL | Netherlands |
| BF | Burkina Faso | GR | Greece | NO | Norway |
| BG | Bulgaria | HU | Hungary | NZ | New Zealand |
| BJ | Benin | IE | Ireland | PL | Poland |
| BR | Brazil | IT | Italy | PT | Portugal |
| BY | Belarus | JP | Japan | RO | Romania |
| CA | Canada | KP | Democratic People's Republic of Korea | RU | Russian Federation |
| CF | Central African Republic | KR | Republic of Korea | SD | Sudan |
| CG | Congo | KZ | Kazakhstan | SE | Sweden |
| CH | Switzerland | LI | Liechtenstein | SI | Slovenia |
| CI | Côte d'Ivoire | LK | Sri Lanka | SK | Slovak Republic |
| CM | Cameroon | LU | Luxembourg | SN | Senegal |
| CN | China | LV | Latvia | TD | Chad |
| CS | Czechoslovakia | MC | Monaco | TC | Togo |
| CZ | Czech Republic | MG | Madagascar | UA | Ukraine |
| DE | Germany | ML | Mali | US | United States of America |
| DK | Denmark | MN | Mongolia | UZ | Uzbekistan |
| ES | Spain | | | VN | Viet Nam |
| FI | Finland | | | | |

Additives and Fuel Compositions

This invention relates to the use of additives for improving the cold flow properties of crude oil, lubricating oil or fuel oil, for example distillate petroleum fuel such as middle distillate fuel oil boiling within the range of 110°C to 500°C.

When oils and fuel oils are subjected to low ambient temperatures, wax may separate out from the fuel and impair the flow properties of the oil. For example, middle distillate fuels contain wax which precipitates at low temperatures to form large waxy crystals which tend to plug the small pore openings of fuel filters. This problem is particularly acute when the fuel is a diesel fuel because the nominal apertures in the fuel filter of diesel engines are typically of diameter between about 5 and 50 microns. Additives are known in the art for overcoming the above problem and are called Flow Improvers.

Such additives may act as wax crystal modifiers when blended with waxy mineral oil by modifying the shape and size of crystals of the wax therein and reducing the adhesive forces between the crystals and between the wax and the oil to permit the oil to remain fluid at a lower temperature than in the absence of the additive.

EP-A-0 261 957 describes the use of additives for improving the cold flow properties of distillate fuels, and exemplifies an additive (designated Additive C therein) comprising the reaction product of one mole of phthalic anhydride with two moles of dihydrogenated tallow amine, to form a half amide/half amine salt, in combination with an additive (designated Additives A therein) comprising an ethylene-vinyl acetate copolymer or a mixture of two ethylene-vinyl acetate copolymers. Specific examples of Additives A used with Additive C in EP-A-0 261 957 are:

Additive A1, which is a 1:3 (w/w) mixture of two copolymers, one being A2 as defined below and the other being A3 as defined below. Thus, the average vinyl acetate content of A1 is 32.75 wt%, i.e. 13.7 mole%;

Additive A2, which is a copolymer consisting of ethylene and about 17 wt% vinyl acetate and having an \bar{M}_n of about 3000 as measured by Vapour Phase Osmometry (VPO), i.e. 6.25 mole% of vinyl acetate;

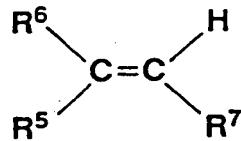
Additive A3, which is a copolymer consisting of ethylene and about 38 wt% vinyl acetate and having an \bar{M}_n of about 1800 as measured by VPO, i.e. 16.6 mole% of vinyl acetate; and

5 Additive A4, which is a 50:50 mixture of Additives A2 and A3 as defined above, the average vinyl acetate content of A4 therefore being 27.5 wt%, i.e. 11 mole%.

10 \bar{M}_n in this specification is the number average molecular weight and is as measured by Gel Permeation Chromatography (GPC) against polystyrene standards unless otherwise stated.

15 A problem in the use of the above-exemplified additives is that the Additives A, although having good performance themselves for improving the cold flow properties of middle distillate fuels, do not necessarily give good cold flow properties when used in combination with Additive C. The present invention meets the problem by employing additives that have a specified mole per cent of a comonomer such as vinyl acetate, the use of additives having such specified mole% giving rise to unexpected and surprising advantages over use of 20 comparison additives in the cold flow properties of middle distillate fuel oils as will be illustrated in the examples hereinafter.

25 Thus, in one aspect, the invention provides an additive comprising one or more oil-soluble copolymers of ethylene and an unsaturated monomer of the general formula



wherein R⁶ is hydrogen or methyl,

30 R⁵ is a -OOCR⁸ group wherein R⁸ is a hydrogen formate or a C₁ to C₂₈, more usually C₁ to C₁₇, and preferably a C₁ to C₈, straight or branched chain alkyl group, or R⁵ is a -COOR⁸ group wherein R⁸ is as defined above but is not hydrogen, and R⁷ is hydrogen or -COOR⁸ as defined above, and wherein

- (i) where there is more than one copolymer, the arithmetic mean of the content of said unsaturated monomer in the copolymers is below 11 mole%, or
- 5 (ii) where there is one copolymer, the content of said unsaturated monomer in the copolymer is in the range of 6.5 to 11, preferably 10, mole%.

In a second aspect, the invention provides the use of an additive of the first aspect of the invention for improving the cold flow properties of crude oil, 10 lubricating oil or a fuel oil such as a middle distillate fuel oil.

In a third aspect, the invention provides a composition comprising an admixture of a major proportion of a crude oil, lubricating oil or a fuel oil such as a middle distillate fuel oil and a minor proportion of an additive of the first aspect of the 15 invention.

In a fourth aspect, the invention provides a concentrate comprising an admixture of an additive of the first aspect of the invention dispersed in a liquid medium compatible with a crude oil, lubricating oil or a fuel oil such as a middle distillate 20 fuel oil.

The features of the invention will now be discussed in further detail.

ADDITIVE

25 Said unsaturated monomer may include alcohol esters of C₁ to C₅ mono-carboxylic acids, such as C₂ to C₅ mono-carboxylic acids. Examples of the monomer include vinyl acetate, vinyl propionate, vinyl butyrate or isobutyrate, vinyl hexanoate and vinyl octanoate, where vinyl acetate and vinyl propionate 30 are preferred. It is preferred that the copolymers have a number average molecular weight as measured by vapour phase osometry of 1,000 to 10,000, preferably 1,000 to 5,000. If desired, the copolymer may be derived from additional comonomers, e.g. it may be a terpolymer or tetrapolymer or higher, for example where the additional comonomer is an iso-olefin such as isobutylene or 35 di-isobutylene.

When there is more than one copolymer, the arithmetic mean of the content of said unsaturated monomer is preferably from 5 to 10 mole%, more preferably 6 to 10 mole%, such as 7 or 8 to 10 mole%.

5 When there is one polymer, the content of said unsaturated monomer is preferably from 7 to 10 mole%, more preferably 8 to 10 mole%, most preferably 8 to 9 mole%.

Such copolymers may be made by copolymerising ethylene and said
10 unsaturated monomer. They may also be made by transesterification, or by hydrolysis and re-esterification, of an ethylene unsaturated ester copolymer to give a different ethylene unsaturated ester copolymer. For example, ethylene vinyl hexanoate and ethylene vinyl octanoate copolymers may be made in this way, e.g. from an ethylene vinyl acetate copolymer.

15

OIL

The oil may be a crude oil, i.e. oil obtained directly from drilling and before refining, the compounds of this invention being suitable for use as flow
20 improvers or dewaxing aids therein.

The oil may be a lubricating oil which may be an animal, fruit, vegetable or mineral oil, such as petroleum oil fractions ranging from naphthas or spindle oil to SAE 30, 40 or 50 lubricating oil grades, castor oil, fish oils or oxidised mineral oil. Such an oil may contain additives depending on its intended use; examples are viscosity index improvers such as ethylene-propylene copolymers, succinic acid based dispersants, metal containing dispersant additives and zinc dialkyl-dithiophosphate antiwear additives. The additives of this invention may be suitable for use in lubricating oils as flow improvers, pour point depressants or
30 dewaxing aids.

The oil may be fuel oil such as a petroleum-based fuel oil, suitably a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of about 110°C to about 500°C, e.g. 150°C to about 400°C. The fuel oil can comprise atmospheric distillate or vacuum distillate, or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. The most common petroleum distillate fuels are kerosene, jet fuels, diesel fuels,

heating oils and heavy fuel oils. The heating oil may be a straight atmospheric distillate, or it may contain minor amounts, e.g. up to 35 wt%, of vacuum gas oil or cracked gas oils or of both. The above-mentioned low temperature flow problem is most usually encountered with diesel fuels and with heating oils. The 5 invention is also applicable to vegetable- or other plant-based fuel oils, for example rape seed oil (e.g. as its methyl ester).

The concentration of the additive in the oil may for example be 10 to 2,000 ppm of additive (active ingredient) by weight per weight of fuel, such as 50, preferably 10 25 to 500 ppm, more preferably 100 to 200 ppm. The additive concentration may include co-additives such as described hereinafter.

The additive should be soluble in the oil to the extent of at least 1000 ppm by weight per weight of oil at ambient temperature. However, at least some of the 15 additive may precipitate from solution near the cloud point of the oil in order to modify the wax crystals that form.

The ratio of the additive to any co-additive such as described hereinafter may for example be in the range of 20:1 to 1:20, such as 10:1 to 1:10, preferably 5:1 to 20 1:5, all ratios being weight:weight.

CO-ADDITIVES

The additives of the invention may, as indicated above, be used in combination 25 with one or more oil-soluble co-additives for improving the cold flow properties of crude oil, lubricating oil or fuel oil. Examples of such co-additives may be selected from polar nitrogen compounds, comb polymers, polyoxyalkylene compounds, hydrocarbon polymers, and sulphur carboxy compounds. Such co-additives will now be discussed in further detail.

30

(i) Polar Nitrogen Compounds

Oil-soluble polar nitrogen compounds may be ionic or dipolar and may comprise for example one or more of the compounds (A) to (B) as follows:

(A) An amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of a hydrocarbyl acid having 1 to 4 carboxylic acid groups or its anhydride.

5 Ester/amides may be used containing 30 to 300, preferably 50 to 150, total carbon atoms. These nitrogen compounds are described in US Patent 4 211 534. Suitable amines are usually long chain C₁₂-C₄₀ primary, secondary, tertiary or quaternary amines or mixtures thereof but shorter chain amines may be used provided the resulting nitrogen
10 compound is oil soluble and therefore normally contains about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C₈ to C₄₀, preferably C₁₄ to C₂₄ alkyl segment.

15 Suitable amines include primary, secondary, tertiary or quaternary, but preferably are secondary. Tertiary and quaternary amines can only form amine salts. Examples of amines include tetradecyl amine, cocoamine, and hydrogenated tallow amine. Examples of secondary amines include dioctadecyl amine and methyl-behenyl amine. Amine mixtures are also suitable such as those derived from natural materials. A preferred amine
20 is a secondary hydrogenated tallow amine of the formula HNR¹R² where in R¹ and R² are alkyl groups derived from hydrogenated tallow fat composed of approximately 4% C₁₄, 31% C₁₆, 59% C₁₈.

25 Examples of suitable carboxylic acids and their anhydrides for preparing the nitrogen compounds include cyclohexane 1,2 dicarboxylic acid, cyclohexene 1,2 dicarboxylic acid, cyclopentane 1,2 dicarboxylic acid and naphthalene dicarboxylic acid, and 1,4-dicarboxylic acids including dialkyl spirobislactone. Generally, these acids have about 5-13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention
30 are benzene dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid. Phthalic acid or its anhydride is particularly preferred. The particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of dihydrogenated tallow amine. Another preferred compound is
35 the diamide formed by dehydrating this amide-amine salt.

Other examples are long chain alkyl or alkylene substituted dicarboxylic acid derivatives such as amine salts of monoamides of substituted succinic acids, examples of which are known in the art and described in US-A-4 147 520, for example. Suitable amines may be those described above.

5

Other examples are condensates such as described in EP-A-327,423.

10 (B) A chemical compound comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system



(I)

15 where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R¹ and R² are the same or different and each is independently a hydrocarbyl group containing 9 to 40 carbon atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof.

20

Preferably, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group.

25

"Hydrocarbyl" in this specification means an organic moiety composed of hydrogen and carbon which, unless the context states otherwise, may be aliphatic, including alicyclic; aromatic; or any combination thereof. It may be substituted or unsubstituted alkyl, aryl or aralkyl and may optionally contain unsaturation. Examples where it is substituted are oxy-, halogeno- and hydroxy-hydrocarbyl.

30

35

The cyclic ring system may include homocyclic, heterocyclic, or fused polycyclic assemblies, or a system where two or more such cyclic assemblies are joined to one another and in which the cyclic assemblies may be the same or different. Where there are two or more such cyclic assemblies, the substituents of the general formula (I) may be on the same or different assemblies, preferably on the same assembly.

Preferably, the or each cyclic assembly is aromatic, more preferably a benzene ring. Most preferably, the cyclic ring system is a single benzene ring when it is preferred that the substituents are in the ortho or meta positions, which benzene ring may be optionally further substituted.

5

The ring atoms in the cyclic assembly or assemblies are preferably carbon atoms but may for example include one or more ring N, S or O atom, in which case or cases the compound is a heterocyclic compound.

10

Examples of such polycyclic assemblies include

15

(a) condensed benzene structures such as naphthalene, anthracene, phenanthrene, and pyrene;

20

(b) condensed ring structures where none of or not all of the rings are benzene such as azulene, indene, hydroindene, fluorene, and diphenylene;

(c) rings joined "end-on" such as diphenyl;

25

(d) heterocyclic compounds such as quinoline, indole, 2:3 dihydroindole, benzofuran, coumarin, isocoumarin, benzothiophen, carbazole and thiadiphenylamine;

30

(e) non-aromatic or partially saturated ring systems such as decalin (i.e. decahydronaphthalene), α -pinene, cardinene, and bornylene; and

(f) three-dimensional structures such as norbornene, bicycloheptane (i.e. norbornane), bicyclooctane, and bicyclooctene.

35

Each hydrocarbyl group constituting R¹ and R² (Formula I) may for example be an alkyl or alkylene group or a mono- or poly-alkoxyalkyl group. Preferably, each hydrocarbyl group is a straight chain alkyl group. The number of carbon atoms in each hydrocarbyl group is preferably 16 to 40, more preferably 16 to 24.

Also, it is preferred that the cyclic system is substituted with only two substituents of the general formula (I) and that A is a methylene group.

5 Examples of salts of the chemical compounds are the acetate and the hydrochloride.

The compounds may conveniently be made by reducing the corresponding amide which may be made by reacting a secondary amine with the appropriate acid chloride; and

10

(C) A condensate of long chain primary or secondary amine with a carboxylic acid-containing polymer.

15

Specific examples include polymers such as described in GB-A-2,121,807, FR-A-2,592,387 and DE-A-3,941,561; and also esters of telemer acid and alkanoloamines such as described in US-A-4,639,256; and the reaction product of an amine containing a branched carboxylic acid ester, an epoxide and a mono-carboxylic acid polyester such as described in US-A-4,631,071.

20

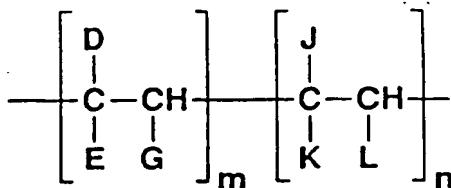
(ii) **Comb Polymers**

Such polymers are polymers in which hydrocarbyl groups are pendant from a polymer backbone and are discussed in "Comb-Like Polymers. Structure and 25 Properties", N A Platé and V P Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

Advantageously, the comb polymer is a homopolymer having, or a copolymer at 30 least 25 and preferably at least 40, more preferably at least 50, molar per cent of the units of which have, side chains containing at least 6, and preferably at least 10, atoms.

As examples of preferred comb polymers there may be mentioned those of the general formula:

10



wherein D = R¹¹, COOR¹¹, OCOR¹¹, R¹²COOR¹¹, or OR¹¹,

E = H, CH₃, D, or R¹²

5 G = H or D

J = H, R¹², R¹²COOR¹¹, or an aryl or heterocyclic group,

K = H, COOR¹², OCOR¹², OR¹², or COOH,

L = H, R¹², COOR¹², OCOR¹², COOH, or aryl,

R¹¹ ≥ C₁₀ hydrocarbyl,

10 R¹² ≥ C₁ hydrocarbyl,

and m and n represent mole ratios, m being within the range of from 1.0 to 0.4, n being in the range of from 0 to 0.6. R¹¹ advantageously represents a hydrocarbyl group with from 10 to 30 carbon atoms, while R¹² advantageously represents a hydrocarbyl group with from 1 to 30 carbon atoms.

The comb polymer may contain units derived from other monomers if desired or required. It is within the scope of the invention to include two or more different comb copolymers.

20 These comb polymers may be copolymers of maleic anhydride or fumaric acid and another ethylenically unsaturated monomer, e.g. an α-olefin or an unsaturated ester, for example, vinyl acetate. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g. maleic anhydride, include 1-decene, 1-dodecene, 25 1-tetradecene, 1-hexadecene, and 1-octadecene.

30 The copolymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols which may be used include n-hexadecan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and n-octadecan-1-ol. The alcohols may also include up to one methyl branch per chain, for example, 1-methylpentadecan-1-ol, 2-methyltridecan-1-ol. The

alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than the commercially available alcohol mixtures but if mixtures are used the R¹² refers to the average number of carbon atoms in the alkyl group; if alcohols that contain a branch at the 1 or 2 positions 5 are used R¹² refers to the straight chain backbone segment of the alcohol.

These comb polymers may especially be fumarate or itaconate polymers and copolymers such for example as those described in European Patent Applications 153176, 153177 and 225688, and WO 91/16407.

10 Particularly preferred fumarate comb polymers are copolymers of alkyl fumarates and vinyl acetate, in which the alkyl groups have from 12 to 20 carbon atoms, more especially polymers in which the alkyl groups have 14 carbon atoms or in which the alkyl groups are a mixture of C₁₄/C₁₆ alkyl groups, made, for example, 15 by solution copolymerizing an equimolar mixture of fumaric acid and vinyl acetate and reacting the resulting copolymer with the alcohol or mixture of alcohols, which are preferably straight chain alcohols. When the mixture is used it is advantageously a 1:1 by weight mixture of normal C₁₄ and C₁₆ alcohols. Furthermore, mixtures of the C₁₄ ester with the mixed C₁₄/C₁₆ ester may 20 advantageously be used. In such mixtures, the ratio of C₁₄ to C₁₄/C₁₆ is advantageously in the range of from 1:1 to 4:1, preferably 2:1 to 7:2, and most preferably about 3:1, by weight.

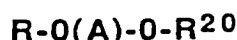
25 Other suitable comb polymers are the polymers and copolymers of α -olefins and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid; mixtures of two or more comb polymers may be used in accordance with the invention and, as indicated above, such use may be advantageous.

30 (iii) **Polyoxyalkylene Compounds**

Examples are polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two C₁₀ to C₃₀ linear saturated alkyl groups and a polyoxyalkylene glycol group of molecular 35 weight up to 5,000 preferably 200 to 5,000, the alkyl group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms. These materials

form the subject of European Patent Publication 0 061 895 A2. Other such additives are described in United States Patent 4 491 455.

5 The preferred esters, ethers or ester/ethers which may be used may be
 5 structurally depicted by the formula



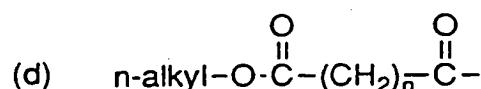
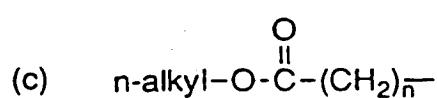
where R and R²⁰ are the same or different and may be

10

(a) n-alkyl



15



20

n being, for example, 1 to 30, the alkyl group being linear and saturated and containing 10 to 30 carbon atoms, and A representing the polyalkylene segment of the glycol in which the alkylene group has 1 to 4 carbon atoms, such as polyoxymethylene, polyoxyethylene or polyoxytrimethylene moiety which is substantially linear; some degree of branching with lower alkyl side chains (such as in polyoxypropylene glycol) may be tolerated but it is preferred that the glycol should be substantially linear. A may also contain nitrogen.

25

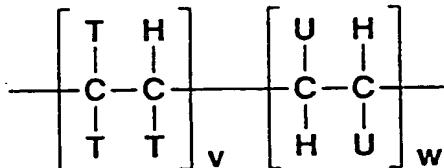
Suitable glycols generally are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000, preferably about 200 to 2,000. Esters are preferred and fatty acids containing from 10-30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use a C₁₈-C₂₄ fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred for use in narrow boiling distillates when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is important for additive 5 performance that a major amount of the dialkyl compound is present. In particular, stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

Examples of other compounds in this general category are those described in 10 Japanese Patent Publication Nos 2-51477 and 3-34790, and the esterified alkoxyated amines described in EP-A-117,108 and EP-A-326,356.

(iv) **Hydrocarbon Polymers**

15 Examples are those represented by the following general formula



where T = H or alkyl

20 U = H, T or Aryl

v = 1.0 to 0.0 (mole ratio)

w = 0.0 to 1.0 (mole ratio)

These polymers may be made directly from ethylenically unsaturated monomers 25 or indirectly by hydrogenating the polymer made from monomers such as isoprene, butadiene etc.

Preferred hydrocarbon polymers are copolymers of ethylene and at least one α -olefin, having a number average molecular weight of at least 30,000. Preferably 30 the α -olefin has at most 20 carbon atoms. Examples of such olefins are propylene, 1-butene, isobutene, n-octene-1, isooctene-1, n-decene-1, and n-dodecene-1. The copolymer may also comprise small amounts, e.g. up to 10% by weight of other copolymerizable monomers, for example olefins other than α -olefins, and non-conjugated dienes. The preferred copolymer is an

ethylene-propylene copolymer. It is within the scope of the invention to include two or more different ethylene- α -olefin copolymers of this type.

The number average molecular weight of the ethylene- α -olefin copolymer is, as indicated above, at least 30,000, as measured by gel permeation chromatography (GPC) relative to polystyrene standards, advantageously at least 60,000 and preferably at least 80,000. Functionally no upper limit arises but difficulties of mixing result from increased viscosity at molecular weights above about 150,000, and preferred molecular weight ranges are from 60,000 and 80,000 to 120,000.

Advantageously, the copolymer has a molar ethylene content between 50 and 85 per cent. More advantageously, the ethylene content is within the range of from 57 to 80%, and preferably it is in the range from 58 to 73%; more preferably from 62 to 71%, and most preferably 65 to 70%.

Preferred ethylene- α -olefin copolymers are ethylene-propylene copolymers with a molar ethylene content of from 62 to 71% and a number average molecular weight in the range 60,000 to 120,000, especially preferred copolymers are ethylene-propylene copolymers with an ethylene content of from 62 to 71% and a molecular weight from 80,000 to 100,000.

The copolymers may be prepared by any of the methods known in the art, for example using a Ziegler type catalyst. The polymers should be substantially amorphous, since highly crystalline polymers are relatively insoluble in fuel oil at low temperatures.

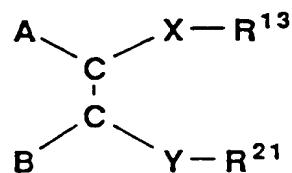
The additive composition may also comprise a further ethylene- α -olefin copolymer, advantageously with a number average molecular weight of at most 7500, advantageously from 1,000 to 6,000, and preferably from 2,000 to 5,000, as measured by vapour phase osmometry. Appropriate α -olefins are as given above, or styrene, with propylene again being preferred. Advantageously the ethylene content is from 60 to 77 molar per cent although for ethylene-propylene copolymers up to 86 molar per cent by weight ethylene may be employed with advantage.

Examples of hydrocarbon polymers are described in WO-A-9 111 488.

(v) Sulphur Carboxy Compounds

Examples are those described in EP-A-0,261,957 which describes the use of compounds of the general formula

5



in which $-Y-R^{21}$ is $SO_3^{(-)}(+)-NR_3^3R^2$, $-SO_3^{(-)}(+)-HNR_2^3R^{21}$,

10 $-SO_3^{(-)}(+)-H_2NR^3R^{21}$, $-SO_3^{(-)}(+)-H_3NR^{21}$,

$-SO_2NR^3R^{21}$ or $-SO_3R^{21}$;

15 $-X-R^{13}$ is $-Y-R^{21}$ or $-CONR^3R^{13}$,

$-CO_2^{(-)}(+)-NR_3^3R^{13}$, $-CO_2^{(-)}(+)-HNR_2^3R^{13}$,

$-R^4-COOR^{13}$, $-NR^3COR^{13}$,

20 $-R^4OR^{13}$, $-R^4OCOR^{13}$, $-R^4R^{13}$,

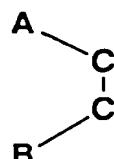
$-N(COR^3)R^{13}$ or $Z^{(-)}(+)-NR_3^3R^{13}$;

25 $-Z^{(-)}$ is $SO_3^{(-)}$ or $-CO_2^{(-)}$;

R^{13} and R^{21} are alkyl, alkoxyalkyl or polyalkoxyalkyl containing at least 10 carbon atoms in the main chain;

30 R^3 is hydrocarbyl and each R^3 may be the same or different and R^4 is absent or

is C_1 to C_5 alkylene and in



the carbon-carbon (C-C) bond is either a) ethylenically unsaturated when A and

35 B may be alkyl, alkenyl or substituted hydrocarbyl groups or b) part of a cyclic

structure which may be aromatic, polynuclear aromatic or cyclo-aliphatic, it is preferred that X-R¹ and Y-R² between them contain at least three alkyl, alkoxyalkyl or polyalkoxyalkyl groups.

- 5 Multicomponent additive systems may be used and the ratios of additives to be used will depend on the fuel to be treated.

CONCENTRATE

- 10 The concentrates of the present invention are convenient as a means for incorporating the additive into bulk oil such as distillate fuel, which incorporation may be done by methods known in the art. The concentrates may also contain other additives as required and preferably contain from 3 to 75 wt%, more preferably 3 to 60 wt%, most preferably 10 to 50 wt% of the additives preferably in solution, in a carrier liquid as the liquid medium. Examples of carrier liquid are organic solvents including hydrocarbon solvents, for example petroleum fractions such as naphtha, kerosene, diesel and heater oil; aromatic hydrocarbons such as aromatic fractions, e.g. those sold under the 'SOLVESSO' tradename; and paraffinic hydrocarbons such as hexane and pentane. The carrier liquid must, of course, be selected having regard to its compatibility with the additive and with the oil.
- 15
- 20

- 25 The additives of the invention may be incorporated into bulk oil by other methods such as those known in the art. If co-additives are required, they may be incorporated into the bulk oil at the same time as the additives of the invention or at a different time.

- 30 The additives of this invention may be used in the presence of various other additives that are commonly used in fuel compositions. Examples of such other additives are rust inhibitors, dyes, detergents, demulsifiers, dispersants, antioxidants, antistatic agents, metal deactivators, cetane improvers and antismoke agents. Such other additives may be present in amounts of about 0.001 to 5 wt%.

EXAMPLES

The invention will now be particularly described by way of example only, as follows.

5

ADDITIVES

The following additives were used.

10 **Ethylene-Vinyl Acetate Copolymers (Additives A-E and K-S)**

| Additive Code | Copolymer I | | Copolymer II | | Average Vinyl Acetate Content (mole%) |
|---------------|-------------------------------|---------------------|-------------------------------|---------------------|---------------------------------------|
| | Vinyl Acetate Content (mole%) | % in Additive (wt%) | Vinyl Acetate Content (mole%) | % in Additive (wt%) | |
| A | 15.5 | 100 | | | 15.5 |
| B | 4.6 | 100 | | | 4.6 |
| C | 15.5 | 75 | 4.6 | 25 | 12.4 |
| D | 15.5 | 50 | 4.6 | 50 | 9.7 |
| E | 15.5 | 25 | 4.6 | 75 | 7.1 |

Thus, Additives A and B comprise a single copolymer whereas Additives C, D and E comprise two copolymers.

15

Also, the following additives, each in the form of a single ethylene-vinyl acetate copolymer, were used.

| Additive Code | Average Vinyl Acetate Content (mole%) |
|---------------|---------------------------------------|
| K | 16.6 |
| L | 11.1 |
| M | 10.2 |
| N | 8.5 |
| O | 7.7 |
| P | 6.5 |
| Q | 4.8 |
| R | 3.8 |
| S | 3.2 |

The following were used as co-additives.

5 **Polar Nitrogen Compound (Additive F)**

An N,N-dialkylammonium salt of 2-N',N'-dialkylamido-benzoate, being the reaction product of reacting one mole of phthalic anhydride with two moles of dihydrogenated tallow amine to form a half amide/half amine salt.

10

Comb Polymer (Additive G)

An itaconate polymer of number average molecular weight about 4000 as measured by Gel Permeation Chromatography (GPC) prepared by polymerising 15 a monomer in a cyclohexane solvent using a free radical catalyst, the monomer containing linear alkyl groups of 16 carbon atoms.

Comb Polymer (Additive H)

20 As Additive G but wherein the monomer contains linear alkyl groups of 18 carbon atoms.

Comb Polymer (Additive I)

25 A copolymer of a dialkyl fumarate, having an \bar{M}_n of about 9500, obtained by reacting fumaric acid with a commercially available alcohol containing primary

n-C₁₄ and n-C₁₅ alcohols and a small quantity of the 2-methyl analogue of the alcohols, and then copolymerising with vinyl acetate in a 1:1 mole ratio.

Comb Polymer (Additive J)

5

A copolymer of a dialkyl fumarate, having an \bar{M}_n of about 15000, obtained by reacting fumaric acid with a n-C₁₄ alcohol and then copolymerising with vinyl acetate in a 1:1 mole ratio.

10 FUELS

The following fuels were used having the indicated characteristics:

| Code | % Wax (wt/wt) (at 10°C below CP) | CP (Cloud Point) (°C) | D-86 Distillation (°C) | | | | |
|------|--|--------------------------|------------------------|-----|-----|-----|-----|
| | | | IBP | 20% | 50% | 90% | FBP |
| 1 | 2.4 | -4 | 140 | 208 | 250 | 334 | 360 |
| 2 | 1.1 | 6 | 187 | 224 | 271 | 370 | 392 |
| 3 | 2.2 | -8 | 138 | 202 | 238 | 327 | 366 |

15 **KEY:** IBP is Initial Boiling Point

FBP is Final Boiling Point

x% is the temperature at which x% of the fuel by volume had distilled.

TESTS

20

Additives were dissolved in the fuels and the following tests carried out on untreated fuel and on fuel treated with additives, some of which were additives of the invention and some of which were not, i.e. they were used for comparison.

25 (a) Cold Filter Plugging Point (CFPP)

The test was carried out by the procedure described in detail in "Journal of the Institute of Petroleum", Volume 52, Number 510, June 1966, pp. 173-285. This test is designed to correlate with the cold flow of a middle distillate fuel oil in automotive diesel engines. A lower CFPP value

30

indicates a superior performance to a higher value in each table of test results below.

(b) Extended Programme Cooling Test (XPCT)

5

The test is a slow cooling test designed to indicate whether the wax in the fuel will pass through filters such as those found in heating oil distribution systems.

10

In the test, the cold flow properties of the described fuels containing the additives were determined as follows. 300 ml of fuel were cooled linearly at 2°C/hour to the test temperature and the temperature then held constant. Wax which had settled in the bottle was dispersed by gentle stirring, then a Cold Filter Plugging Point (CFPP) filter assembly, which is described in detail in "Journal of the Institute of Petroleum", Volume 52, Number 510, June 1966, pp. 173-285, inserted. The tap was opened to apply a vacuum of 500 mm of mercury and closed when 200 ml of fuel had passed through the filter into the graduated receiver. A PASS was recorded if the 200 ml passed through a given mesh size or a FAIL if the filter became blocked.

20

A series of CFPP filter assemblies with filter screens of different sizes including LTFT (AMS 100.65) and a Volkswagen Tank filter (part no KA/4-270/65.431-201-511) both intermediate between 30 and 40 µm were used to determine the finest mesh the fuel will pass. The sizes of the filter screens were as follows in order of increasing size, i.e. in order of decreasing severity as a test: 10 µ, 15 µ, 20 µ, 25 µ, 500, LTFT, 350, VW, 250, 200, 150, 120, 100, 80, 60, 40 and 30, where figures alone indicate mesh sizes. To assist comparison, results in each table are rated in numerical order where a lower number indicates a superior result to a higher number.

RESULTS

35 The results are shown in the tables below, where additives are referred to by the above-mentioned Additive Codes. EVA means an ethylene-vinyl acetate copolymer in accordance with the Additive Code and VA means vinyl acetate.

Examples marked "comp" are comparative examples.

Table 1

Fuel 1; Treat Rates EVA:200 ppm; F:200 ppm; G:200 ppm without H,
100 ppm with H; H:100 ppm

| Example | EVA; mole% VA | Co-additives | Tests | |
|----------|---------------|--------------|-----------|------------------|
| | | | CFPP (°C) | XPCT (Rating No) |
| BASE | | | -3.5 | 30# |
| 1 (comp) | A 15.5 | F, G | -7.5 | 500# (2) |
| 2 (comp) | C 12.4 | F, G | -9 | LTFT (3) |
| 1 | D 9.7 | F, G | -13.5 | 10μ (1) |
| 2 | E 7.1 | F, G | -10.5 | VW (4) |
| 3 (comp) | A 15.5 | F, G, H | -9 | 500# (4) |
| 4 (comp) | C 12.4 | F, G, H | -10 | 25μ (3) |
| 3 | D 9.7 | F, G, H | -15.5 | 15μ (2) |
| 4 | E 7.1 | F, G, H | -18.0 | 10μ (1) |

5

Table 2
Fuel 3; Treat Rates EVA:60 ppm; F:40 ppm; I:100 ppm

| Example | EVA; mole% VA | Tests | |
|-----------|---------------|-----------|------------------|
| | | CFPP (°C) | XPCT (Rating No) |
| BASE | | -10 | |
| 7 (comp) | K 16.6 | -10.5 | 40# (7) |
| 8 (comp) | L 11.1 | -13 | 80# (1) |
| 10 | N 8.5 | -15 | 80# (1) |
| 11 | O 7.7 | -14.5 | 80# (1) |
| 9 (comp) | Q 4.8 | -12.5 | 80# (1) |
| 10 (comp) | R 3.8 | -12.5 | 60# (5) |
| 11 (comp) | S 3.2 | -12.5 | 60# (5) |

Table 3
Fuel 2; Treat Rates EVA:60 ppm; F:40 ppm

| Example | EVA; mole% VA | Tests | |
|-----------|---------------|-----------|---------------------|
| | | CFPP (°C) | XPCT (Rating No) |
| BASE | | -1 | 200# |
| 12 (comp) | K 16.6 | -4.5 | 200# (6) |
| 13 (comp) | L 11.1 | -3 | 200# (6) |
| 12 | M 10.2 | -4 | 350# (4) |
| 13 | N 8.5 | -4.5 | LTFT (3) |
| 14 | O 7.7 | -5.5 | 25μ (2) |
| 15 | P 6.5 | -4.5 | 350# (4) |
| 14 (comp) | R 3.8 | -2.5 | 20μ (1) |

Table 4
Fuel 2; Treat Rates EVA:60 ppm; F:40 ppm; J:100 ppm

| Example | EVA; mole% VA | Tests | |
|-----------|---------------|-----------|---------------------|
| | | CFPP (°C) | XPCT (Rating No) |
| BASE | | -1 | 200# |
| 15 (comp) | K 16.6 | -4.5 | 200# (6) |
| 16 (comp) | L 11.1 | -15 | 200# (6) |
| 16 | M 10.2 | -17 | 500# (1) |
| 17 | N 8.5 | -18 | 350# (3) |
| 18 | O 7.7 | -18.5 | 500# (1) |
| 19 | P 6.5 | -16 | 350# (3) |
| 17 (comp) | Q 3.8 | -17.5 | 350# (3) |

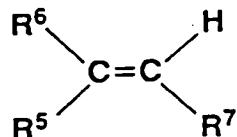
5 The "Base" example is for the fuel as such (i.e. containing no additives).

The examples marked 1 to 19 are examples of the invention and show an improvement in performance over the corresponding comparative example.

Claims:

1. An additive comprising one or more oil-soluble copolymers of ethylene and an unsaturated monomer of the general formula

5



wherein R⁶ is hydrogen or methyl,

10 R⁵ is a -OOCR⁸ group wherein R⁸ is a hydrogen formate or a C₁ to C₂₈, more usually C₁ to C₁₇, and preferably a C₁ to C₈, straight or branched chain alkyl group, or R⁵ is a -COOR⁸ group wherein R⁸ is as defined above but is not hydrogen, and R⁷ is hydrogen or -COOR⁸ as defined above, and wherein

15

(i) where there is more than one copolymer, the arithmetic mean of the content of said unsaturated monomer in the copolymers is below 11 mole%, or

20

(ii) where there is one copolymer, the content of said unsaturated monomer in the copolymer is in the range of 6.5 to 10 mole%.

2. An additive of claim 1 comprising one copolymer wherein the range is 7 to 10 mole%.

25

3. An additive of claim 2 wherein the range is 8 to 10 mole%.

4. An additive of claim 1 comprising more than one copolymer wherein the range is from 5 to 10 mole%.

30

5. An additive of claim 4 wherein the range is from 6 to 10 mole%.

35

6. An additive of any of the preceding claims in combination with one or more co-additives for improving the cold flow properties of crude oil, lubricating oil or fuel oil.

7. An additive of claim 6 wherein the one or more oil-soluble co-additives are selected from a polar nitrogen compound, a comb polymer, a polyoxyalkylene compound, a hydrocarbon polymer, and a sulphur carboxy compound.
- 5 8. An additive of claim 7 wherein the co-additive is a polar nitrogen compound comprising an amine salt or amide or both formed by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of a hydrocarbyl acid having 1 to 4 carboxylic acid groups or its anhydride.
- 10 9. An additive of any of the preceding claims wherein said unsaturated monomer is vinyl acetate or vinyl propionate.
- 15 10. A composition comprising an admixture of a major proportion of a crude oil, lubricating oil or a fuel oil and a minor proportion of an additive of any of the preceding claims.
- 20 11. A composition of claim 10 containing the additive, including the co-additive if present, in a total proportion of from 50 to 500 ppm by weight based on the weight of the oil.
12. A composition of claim 10 or claim 11 wherein the oil is a middle distillate fuel oil.
- 25 13. An additive concentrate comprising an additive of any of claims 1 to 9 in an oil or a solvent miscible with oil.
- 30 14. The use of an additive of any of claims 1 to 9 to improve the low temperature properties of an oil.
15. The use of claim 14 wherein the oil is a fuel oil.
16. The use of claim 15 wherein the fuel oil is a middle distillate fuel oil.

INTERNATIONAL SEARCH REPORT

Int'l. application No.

PCT/EP 93/01669

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C10L 1/14, C10M 145/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPCS: C10L, C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| X | EP, A2, 0177306 (EXXON RESEARCH AND ENGINEERING COMPANY), 9 April 1986 (09.04.86), page 5, line 13 - line 15, claims 1,6 -- | 1,9,10,14-16 |
| X | EP, A1, 0360419 (EXXON CHEMICAL PATENTS INC.), 28 March 1990 (28.03.90), page 7, line 31 - line 34, claims 1,10-12 -- | 1,6,9-11, 14-16 |
| X | EP, A1, 0455206 (SOCIETA' ITALIANA ADDITIVI PER CARBURANTI S.R.L.), 6 November 1991 (06.11.91), claims 1,3,15 -- | 1-6,9,10,12, 14-16 |

 Further documents are listed in the continuation of Box C. See patent family annex.

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "B" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|--|--|
| 15 Sept 1993 | 08.10.93 |
| Name and mailing address of the ISA/EP European Patent Office, P.O. Box 3818 Patendaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Telex 31 651 epo nl. Fax: (+31-70) 340-3016 | Authorized officer INGA-KARIN PETERSSON |

INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 93/01669

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | EP, A1, 0465042 (EXXON RESEARCH AND ENGINEERING COMPANY), 8 January 1992 (08.01.92), page 3, line 47 - page 4, line 11, claims 1-3 -- | 1,6,9,12, 14-16 |
| X | WO, A1, 9116407 (EXXON CHEMICAL LIMITED ET AL.), 31 October 1991 (31.10.91), page 6 - page 9; page 17, line 18 - page 18, line 8 -- ----- | 1-7,9,10,14, 15 |

INTERNATIONAL SEARCH REPORT
Information on patent family members

26/08/93

International application No.
PCT/EP 93/01669

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|--|------------------|-------------------------|----------|------------------|
| EP-A2- 0177306 | 09/04/86 | AU-A- | 4797185 | 10/04/86 |
| | | JP-A- | 61166885 | 28/07/86 |
| EP-A1- 0360419 | 28/03/90 | DE-U- | 6890308 | 05/11/92 |
| | | JP-A- | 2105891 | 18/04/90 |
| EP-A1- 0455206 | 06/11/91 | US-A- | 5189231 | 23/02/93 |
| EP-A1- 0465042 | 08/01/92 | CA-A- | 2042855 | 29/12/91 |
| | | JP-A- | 4226192 | 14/08/92 |
| | | US-A- | 5094666 | 10/03/92 |
| | | US-A- | 5092908 | 03/03/92 |
| WO-A1- 9116407 | 31/10/91 | CN-A- | 1056118 | 13/11/91 |
| | | EP-A- | 0525040 | 03/02/93 |